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BIODIESEL PRODUCTION FROM FISH WASTE AND CHARACTERIZING THE PROPERTIES

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ABSTRACT

Because of the increase in the energy demand in the global world, there is a need to find another source to fossil fuels. Biodiesel is one of the substitute resource since it is biodegradable in nature and causes less pollution. Fish feed stock one of the promising feed is investigated for biodiesel production. The fat extraction was done from fish waste using water as solvent. Then it was saponified with sodium hydroxide to reduce the fatty acid content. The optimization of experimental conditions was done by varying catalyst concentration and reaction temperature. The transesterification reaction was conducted in the presence of a potassium hydroxide catalyst to convert fatty acid ester of one type to another type. The properties of the produced biodiesel were tested as per the ASTM standards and the results were found to be meeting the engine combustion standards.

KEYWORDS: Transesterification, Fish Feed Stock, Optimization, Yield & Biodiesel

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Original Article

INTRODUCTION

Because of industrialization and increase in the population there is a growing demand for consumption of energy sources. The non-renewable sources such as fossil fuels are used at an ever increasing rate in order to meet the demands of the society [1]. Therefore, these resources are getting depleted over a short period of time. At the same time, the fossil fuels threats the environment in the form of global warming, climate change and greenhouse gas emissions [2]. The price of these fuel resources is also increasing in the global market because of its diminishing availability [3]. Thus an alternative source of energy is required for addressing all of the above problems. The other energy sources can be from wind, hydroelectric, geothermal, solar and energy from bio source feed stock [4]. Biodiesel from biosources is an effective alternative source because it is biodegradable, nontoxic, it does not contain any sulfur and causes less pollution [5, 6].

Biodiesel can be produced from different sources such as plant waste, edible oils, used cooking oil, animal waste and refinery waste. Sources such as vegetable oils like palm oil, soybean oil, sunflower oil, groundnut oil and coconut nut are considered as first generation biodiesel [7]. They have very low fatty acid content which is beneficial for biodiesel production [8]. But the use of these sources will lead to problems such as shortage of food supply and starvation [9]. The second generation biodiesel is produced from using cooking oil, non-edible crops and also from other animal waste, poultry waste, beef tallow, pork lard and fish waste. They have higher fatty acid content [10]. Thus fish waste which is found to be easily available at low cost and has a minimum number of uses can be used for biodiesel production.

In the recent time, the fish consumption has increased at a greater rate. Also, because of growing population, growth in income and urbanization have resulted in demand for fish consumption [11]. The literature shows that 75% of total fish produced is used for human consumption while the remaining is used for producing non-food grade such as fish oil [12]. Some of the fish parts such as heads, fins, eyes, tails, viscera and some discarded parts are not eaten and can be grouped as waste [13]. It was also reported that the amount of waste obtained from fish processing plants is about 50% of total processed feed [12]. The fish processing industry releases waste like tissue waste or by-products which can be discarded or can be used for feeding animals [14]. This low cost waste obtained contains around 50% of oil [12].

Fish oil extracted from the most of the fishes contains omega-3 polyunsaturated fatty acids. These fatty acids are made up of Eicosapentaenoic and docosahexaenoicacid. But the vegetable oils contains mainly linoleic acid, linolenic acid, oleic acid and palmitic acid. The chemical components present in fish oil have longer carbon chains when compared to the carbon chain of the components in the vegetable oil. This will help in producing biodiesel with a higher cetane number. It will improve the engine performance and results in less pollution [15]. The research carried out on the production of biodiesel using fish waste as feed stock is limited. The fish waste can be a promising feed for the production of various final products such as biogas, biodiesel and for energy generation [16]. Therefore an attempt has been made to produce biodiesel from fish waste feed stock.

Different technologies such as pyrolysis of oil, micro-emulsion method, fermentation, hydrolysis, extraction, ultrasound assisted, microwave and transesterification processes are used for biodiesel production from feed stock [17, 18]. The biodiesel from the transesterification has better properties like nontoxicity, free from sulfur and aromatics, biodegradable and renewable in nature [19].

Transesterification reaction involves the reaction of triglycerides with any alcohol in the presence of catalyst to produce biodiesel and esters. The ester of one type gets converted to the ester of another type [20].

The reaction can be represented as

$$\text{Oil} + \text{Alcohol} \xleftrightarrow{\text{catalyst}} \text{Ester} + \text{Glycerol}$$

The biodiesel is formed as the light layer at the top and the glycerol obtained as heavy layer at the bottom, which are for producing cosmetics [21]. Different catalysts are used for the transesterification process such as alkali catalyst [22], acid catalyst [23], homogeneous catalyst [24] and heterogeneous catalyst [25] are used for the transesterification reaction. Thus the present study investigates the production of biodiesel from fish waste feed stock. The transesterification reaction was carried out by varying the catalyst concentration and the reaction temperature. The properties of the produced biodiesel were tested as per the ASTM standards.

MATERIALS AND METHODS

Materials

The fish waste feed stock was obtained from a fish processing centre, Malpe and used for the investigation. The fish parts having less value such as tails, heads, organs and fins were used for the biodiesel production. The chemicals potassium hydroxide (Merck India Limited), methanol (Hayman Speciality Products) and sodium hydroxide (Fischer Scientific Limited) were used for the experiments.

Extraction of the Fat and Saponification

The fish processing waste was mixed with water as a solvent and heated inside three neck round bottom flask on a heating mantle (Central Scientific Maxserve) for extracting fish fat. The fish waste was heated for 1 hour at 80^{o}C. Then it is subjected to decantation for 30 minutes for the separation of fat layer. The decantation process was repeated two to three times so that all the fat is separated.10 ml of extracted fat is mixed with 25 ml of 1N sodium hydroxide solution and stirred in an electronic shaker for the saponification reaction. Later the solution is centrifuged in a centrifuge (Eppendorf 5430) at a speed of 3000 rpm for 15 minutes so that all the saponified fat is separated.

Transesterification Reaction

The transesterification reaction was carried out by mixing 87 ml of the saponified fish fat with 17.5 grams of the methanol as alcohol (i.e. 1:5 alcohol to oil ratio) by varying the temperature in the range of 32-60^{o}C, catalyst (KOH) in the concentration of 0.5-2.5% in a magnetic stirrer (1 MLH REMI) for 1 hour. After the reaction, the mixture was placed in a separating funnel for 2.5 hours for separation of biodiesel and glycerol. Later the two layers, the biodiesel formed in the top layer and the bottom layer containing glycerin were separated. Then the separated biodiesel and glycerin were washed two to three times with distilled with in 1:1 ratio to remove the unreacted alcohol. Finally the biodiesel was heated to vaporize the traces of water.

RESULTS AND DISCUSSIONS

Purified Fat Obtained after Saponification Reaction

During the extraction process the fish fat obtained was 964.2 ml over the entire course of the experiment. The fat is subjected to saponification with sodium hydroxide for the removal of fatty acids and the purified fat obtained after the reaction was 875.1 ml.

Optimization of Transesterification Parameters

Influence of Catalyst Concentration on Biodiesel Yield

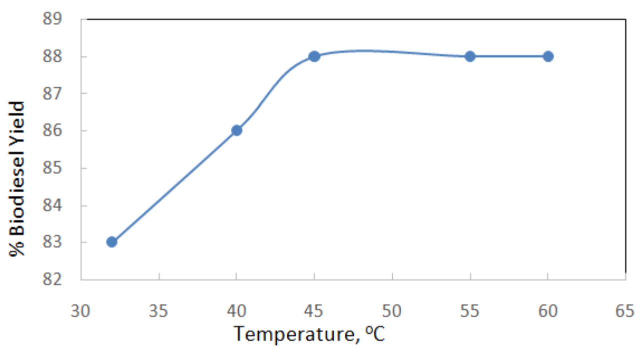

Figure 1: The Influence of Catalyst Concentration on Biodiesel Yield

The effect of KOH concentration was investigated in the range of 0.5 -2.5% (weight of the catalyst / weight of feed) and is shown in figure 1. It was found that the ester formed increases as the amount of catalyst increased from 0.5-1 % and later on it decreases from 1- 2.5%. The percent yield decreased drastically as the catalyst concentration increased above 2%. Thus 0.975 g of catalyst was taken as the optimum concentration. The reason for drop in biodiesel yield with increasing catalyst concentration is because of the reason that higher soap is formed during the reaction [23].

Effect of Temperature on the Transesterification Reaction

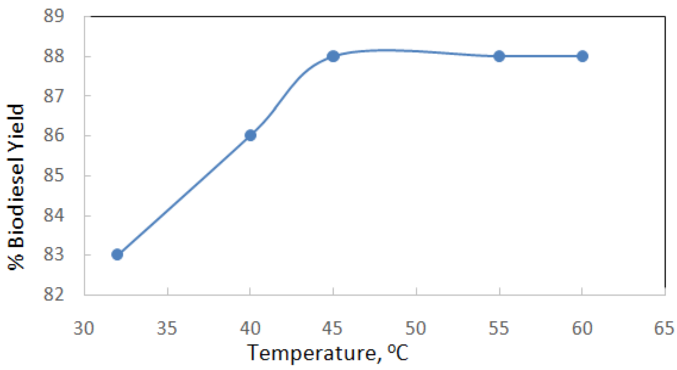

Figure 2: The Influence of Temperature on Biodiesel Yield

The effect of temperature on the biodiesel yield was studied by varying the temperature from 32- 60^{o}C and is given in figure 2. The biodiesel yield after 10 minutes of reaction was measured for all the different temperatures. The yield was highest at 60^{o}C and it was lower at other temperatures. After carrying out the reaction for 1 hour, the yields as shown in the figure are obtained. Thus it can be proved that maximum yield was obtained at the highest temperature of 60^{o}C at all periods of time. Therefore 60^{o}C was taken as the optimum value. This is because of the reason that temperature influences the reaction rate and yield of esters [26].

The transesterification reactions were carried out at the optimum conditions and the values obtained are given in Table 1. The biodiesel yield was calculated from the following formula.

$$Biodiesel\ Yield\ (\%) = \frac{biodiesel\ obtained}{fish\ oil\ taken} \times 100 \quad (1)$$

Table 1: The Biodiesel Yield Obtained Under the Optimum Conditions

Sl. No	Fish Fat (g)	Catalyst (g)	Alcohol (g)	Biodiesel (g)	Glycerol (g)	Biodiesel Yield (%)
1.	87	0.975	17.4	78.131	8.869	89.80
2.	87	0.975	17.4	80.71	6.29	92.77
3.	87	0.975	17.4	79.37	7.63	91.24
4.	87	0.975	17.4	77.34	9.66	88.8

Confirmation for Production of Biodiesel (Jan Warnquisttest)

The confirmation test was performed to calculate the extent to which the triglyceride (feed oil) is converted into fatty acid methyl ester (biodiesel). The test is very important in finding the quality of biodiesel produced. The test is conducted by mixing 25 ml of biodiesel with 225 ml of the alcohol (i.e. 1:9 volume ratio of biodiesel to alcohol) in a test tube. After mixing for 30 minutes it was detected that no oily material settled at the test tube bottom, signifying that highly converted biodiesel was formed [27]. It was also observed that the clear solution was formed at the bottom.

Properties of Biodiesel and Comparison as per the ASTM Standards

The various biodiesel properties like cloud point, flash point, fire point, pour point, kinematic viscosity, sulfur content, fatty acid content were measured as per the ASTM standards [28, 29, 30]. The values were compared with that of petrodiesel properties. The obtained values were found to be promising to fulfil the requirement of engine combustion standards. The fire point and pour point were obtained as 153^{o}C and -9^{o}C respectively. The free fatty acid value for the

feed oil was 0.12% showing that it is a better feed stock for biodiesel production. The saponification value for the biodiesel was 204.7 mg KOH/ 1 g of fat. The comparison of all the other biodiesel properties measured as per the ASTM standards is represented in the Table 2.

Table 2: The Biodiesel Properties Obtained as Per the ASTM Standards

Test Parameter	Result	ASTM Limit	Units	Test Method (current revision)
Cloud point:	3.2 (37.76)	Report	°C (°F)	D 2500
CFPP¹:	0	N/A	°C	D 6371
Free Glycerin:	0.006	0.020 max.	% Mass	D 6584
Total Glycerin:	0.040	0.240 max.	% Mass	D 6584
Monoglycerides²:	0.118	N/A	% Mass	D 6584
Diglycerides³:	0.019	N/A	% Mass	D 6584
Triglycerides⁴:	0.000	N/A	% Mass	D 6584
Water & Sediment:	< 0.005	0.050 max.	% Volume	D 2709
Acid Number:	0.085	0.50 max.	mg KOH/g	D 664, Test Method A
Visual Inspection:	1	N/A	Haze	D 4176, Procedure 2
Relative Density at 60 °F:	0.8955	N/A	N/A	D 1298
Oxidative Stability (110 °C):	0.2	3 min.	hrs	EN 14110
Flashpoint (closed cup):	>160	93 min.	°C	D 93
Moisture⁵:	0.056	N/A	% Mass	E 203
Cold Soak Filtration:	68	360	seconds	D 6751 Annex
Sulfur:	9.3	15	ppm	D 7039
Calcium:	<0.1	5 max. Ca + Mg	ppm (ug/g)	EN 14538
Magnesium:	0.3	5 max. Ca + Mg	ppm (ug/g)	EN 14538
Phosphorus:	<0.1	0.001 max.	% Mass	D 4951
Carbon Residue:	0.078	0.050 max.	% Mass	D 524
Sulfated Ash:	<0.005	0.020 max.	% Mass	D 874
Kinematic Viscosity at 40 °C:	3.777	1.9-6.0	mm^2/sec.	D 445
Copper Corrosion (3 hrs at 50 °C):	1a	No. 3 max.	N/A	D 130

CONCLUSIONS

The need for alternative energy source was addressed in this study by producing biodiesel from fish waste. The extraction of fish oil was carried out using water as a solvent. The saponification of the fat with sodium hydroxide was effective in removing the fatty acids to a lower value. The optimization of the experimental parameters like catalyst concentration and reaction temperature was obtained as 0.975 g of catalyst and 60°C. The transesterification reaction was carried out at the optimum conditions and the biodiesel yield up to 92% was obtained. The various properties of the biodiesel were evaluated using ASTM standards. The produced biodiesel was exhibiting properties which were satisfying the requirement of combustion engines.

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